Sulfate Promoted Zirconia as Promising Alkali-Resistant Support for Catalytic NOx Removal

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Sulfate Promoted Zirconia as Promising Alkali-Resistant Support for Catalytic NO_x Removal

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1. Introduction

THE use of bio-fuels as alternatives to traditional fossil fuels has attracted much attention recent years since bio-fuels belong to a family of renewable types of energy sources and do not contribute to the green-house effect. Selective catalytic reduction (SCR) of NO_x with ammonia as reductant is the most efficient method to eliminate NO_x from flue gases in stationary sources.

The traditional SCR catalyst suffers significant deactivation with time due to the presence of relative large amounts of potassium in bio-fuels. A possible solution to this problem is use of highly acidic supports, which would interact with potassium stronger than active metal species.[1,2]

2. Experimental

THE sample of sulfated zirconia with 4.1 wt% sulfate has been obtained commercially. The as-received support was impregnated with ammonium metavanadate via incipient wetness impregnation and calcined in air at 400°C, resulting in 0.5-7.5 wt% vanadium with a BET surface area of 145 $^{m^2}/_{g}$. The vanadia-based catalysts were impregnated with 130 $^{\mu mol}/_{g}$ KNO_3.

$$\underbrace{SO_4^{2-}/ZrO_2}_{\text{4.1 wt\% } SO_4^{2-}} \xrightarrow[\text{IWI}]{NH_4VO_3} \underbrace{V_2O_5{-}SO_4^{2-}/ZrO_2}_{\text{0.5-7.5 wt\% V}} \xrightarrow[\text{IWI}]{KNO_3} \underbrace{K_2O{-}V_2O_5{-}SO_4^{2-}/ZrO_2}_{\text{K/V = 0.4}} \qquad (1)$$

A 3%V_2O_5-7%WO_3/TiO_2 catalyst with a BET surface area of 61 $^{m^2}/_{g}$ was used as a reference.

NO SCR was performed with 50 mg sample in 1000 ppm NO, 1100 ppm NH_3, 3.5% O_2, and 2.5% H_2O, balanced with N_2, total flow: 300 $^{ml}/_{min}$.

3. Sample Acidity

IMPREGNATION of the sulfated zirconia with vanadia results in an additional ammonia desorption peak around 390°C (Fig. 1). This peak is only observed in vanadia-containing samples on sulfated zirconia and not i.e. in tungstated zirconia[1].

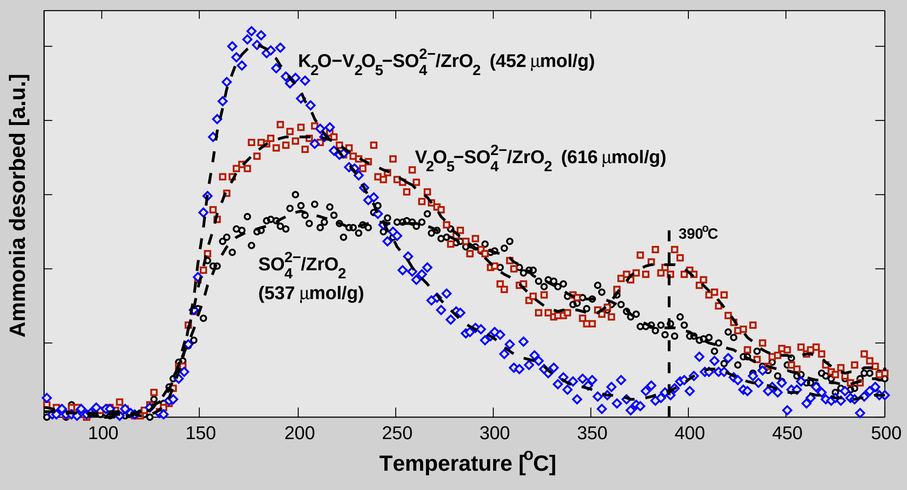

Figure 1: *NH_3-TPD of the sulfated samples (Surface acidity in brackets), indicating a formation of a stronger acid site with addition of 1.7 wt% V*

4. NO SCR Activity

CATALYSTS based on sulfated zirconia exhibit good SCR properties compared with the titania-based reference catalyst, both depicted in Fig. 2. Especially the SCR activity after K-doping reveals the high alkali resistance of sulfated supports over the traditional catalyst, the latter deactivating 71% at 300°C, whereas the sulfated catalyst only deactivates 29%.

Optimization of the vanadia loading was performed to study the catalysts resistance toward a constant amount of potassium (130 $^{\mu mol}/_{g}$). The deactivation of catalysts containing 0.5–7.5 wt% vanadium due to potassium poisoning is depicted in Fig. 4, top.

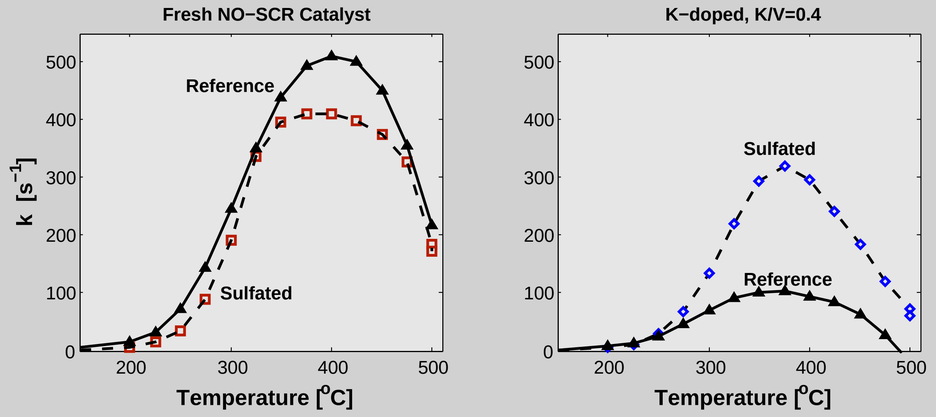

Figure 2: *The temperature dependency of the SCR activity of 3wt% V_2O_5-4.1wt% SO_4^{2-}/ZrO_2 and a 3 wt% V_2O_5-WO_3/TiO_2 reference catalyst*

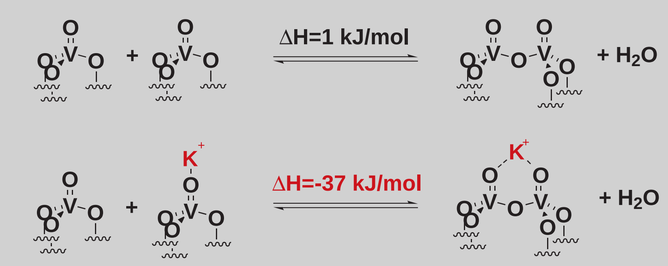

Figure 3: *The propensity for dimerization calculated by DFT. Notice with potassium present, the dimer is now clearly favored in enthalpy[3]*

Increasing the amount of vanadium, thus decreasing the K/V ratio, results in significant decrease in catalyst deactivation (Fig. 4, top left). At K/V = 0.2 only about 10% catalyst deactivation is observed, which even decreased further with increasing vanadium concentration.

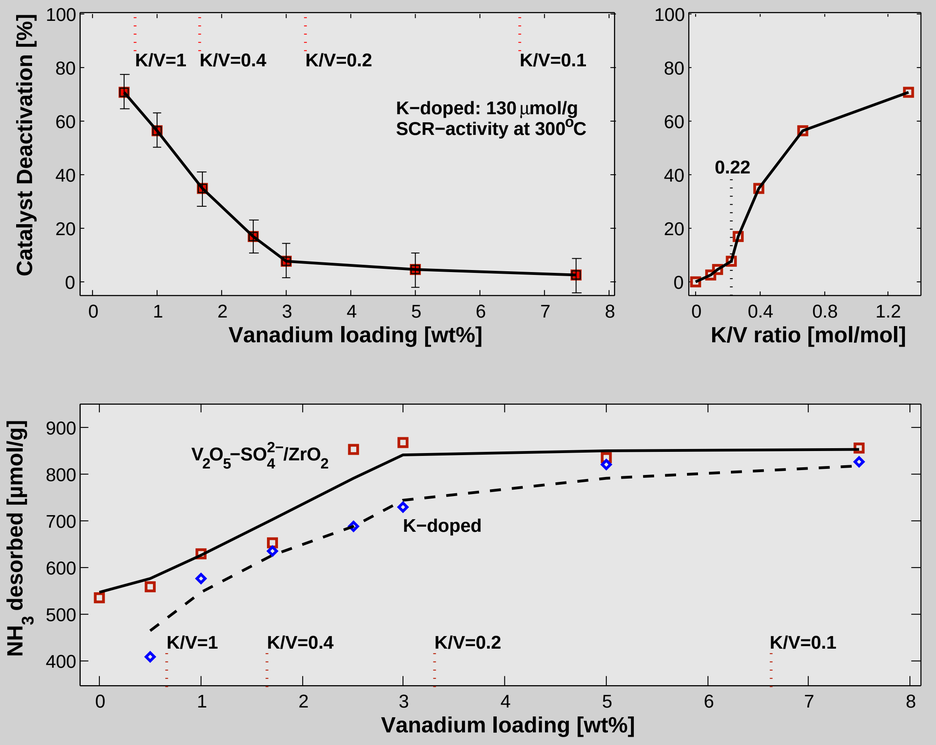

Figure 4: *Top left: Catalyst deactivation with different vanadia loadings at 300°C; Top right: Deactivation versus the K/V molar ratio, with threshold at K/V = 0.22; Bottom: Amount of desorbed NH_3 from the vanadia-impregnated support and the corresponding K-doped samples*

5. Conclusion

CATALYSTS based on sulfated zirconia show good resistance towards potassium poisoning. For samples with K/V ratios below 0.22, potassium seems to have very low impact on the catalysts performance.

Poisoning the catalysts with potassium mainly affects the strong acid sites, with NH_3 desorption temperature around 390°C.

References

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[2] Kustov, A.L., Kustova, M.Y., Fehrmann, R., Simonsen, P., *Appl. Catal. B*, 58 **(2005)** 97–104.

[3] Due-Hansen, J., Boghosian, S., Kustov, A.L. Fristrup, P., Tsilomelekis, G., Ståhl, K., Christensen, C.H., Fehrmann, R., *J. Catal.*, submitted, april 2007.

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